❖ Acids & Bases

- There are 3 definitions of acids and bases:

Arrhenius definition:

Acids donate H^+ in H_2O (H^+ donor)

Bases donate OH^- in water (OH^- donor)

$$HCL_{(aq)} \xrightarrow{H_2O} H^+_{(aq)} + Cl^-_{(aq)}$$

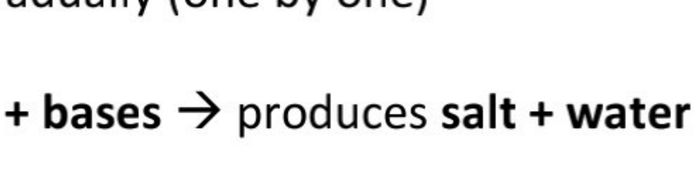
$$NaOH_{(aq)} \xrightarrow{H_2O} Na^+_{(aq)} + OH^-_{(aq)}$$

➢ This definition applied only in aqueous solutions

Bronsted- Lowry definition:

Acids donate H^+ (Proton donor) when dissolved in water **forming H_3O^+**

Bases accept H^+ (Proton acceptor) when dissolved in water **forming OH^-**



Lewis definition:

Acids accept **electrons**

Bases donate **electrons (non-boning pairs of electrons)**

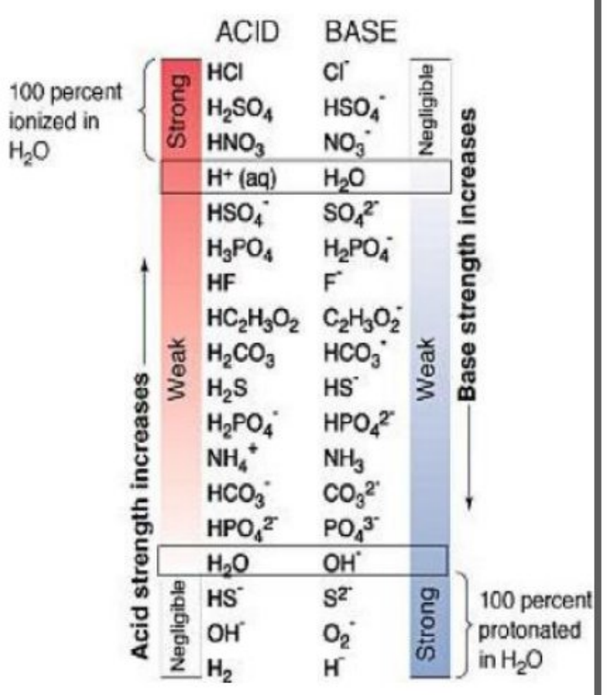
- **Notes:**
  - ➢ Ionization of acids or bases → produce **conjugate** bases or acids
  - ➢ Acids can be classified according to the **number of protons** they can donate:
    - ✓ **Monoprotic acids** (can donate 1 proton) such as HCl, HNO_3, CH_3COOH
    - ✓ **Diprotic acids** (can donate 2 protons) such as H_2SO_4
    - ✓ **Triprotic acids** (can donate 3 protons) H_3PO_3
  - ➢ Protons are donated gradually (one by one)
  - ➢ Neutralization of **acids + bases** → produces **salt + water**
  - ➢ Water is an **amphoteric substance** (can act as an acid in one reaction & as a base in another):
    - ✓ With **bases** (such as ammonia NH_3) water acts as an **acid**

      $NH_3 + H_2O \leftrightarrow NH_4^+ + OH^-$
    - ✓ With **acids** (such as Hydrochloric acid HCl) water acts as a **base**

      $HCl + H_2O \leftrightarrow H_3O^+ + Cl^-$

❖ The strength of Acids & Bases

- Acids and bases differ in their ability to release and accept protons (their strength):
  - ➢ Strong Acids **dissociate completely** 100%
  - ➢ Strong bases have **strong affinity** for proton



- In multi-protic acids each proton is donated at **different strength** (the first donation is the strongest)
- The stronger the acid = the weaker the conjugate base and vise versa
- The reaction of **strong** acid and bases is a **one-way reaction**

  $HCl \rightarrow H^+ + Cl^-$ / $NaOH \rightarrow Na^+ + OH^-$
- **Weak** acids and bases **don't ionize completely** (**Partial/reverse reaction**)

  $HC_2H_3O_2 \leftrightarrow H^+ + C_2H_3O_2$ / $NH_3 + H_2O \leftrightarrow NH_4^+ + OH^-$

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- To deal with the strength of Acids and bases we use K_a & pK_a (for acids), K_b & pk_b (for bases)

❖ K_a (acid dissociation constant) & pK_a

- We can find out this constant using the equilibrium constant (K_{eq}) for the reaction ($HA \leftrightarrow H^+ + A^-$)
- **Equilibrium** is the state when the rate of the forward reaction = the rate of the backward reaction
- HA → the acid / A^- → conjugate base
- **$[H^+] = [H3O^+] = [A^-]$**

- The value of K_a indicates:
  - If K_a is **larger than 1** → the product side is favored → more dissociation → the **acid is strong**
  - If K_a is **smaller than 1** → the reactants side is favored → less dissociation → the **acid is weak**

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

- **$pK_a = -\log K_a$**
  - **K_a is inversely related to pK_a**
  - **Larger K_a → smaller pK_a → more dissociation → stronger acid**

❖ K_b (base dissociation constant) & pK_b

- We can find out this constant using the equilibrium constant (K_{eq}) for ➔ ($B + H2O \leftrightarrow BH^+ + OH^-$)
- B → the base / BH^+ → conjugate acid
- **$[BH^+] = [OH^-]$**

- The value of K_b indicates:
  - If K_b is **larger than 1** → the product side is favored → more ionization → the **base is strong**
  - If K_b is **smaller than 1** → the reactants side is favored → less ionization → the **base is weak**

$$K_b = \frac{[BH^+][OH^-]}{[B]}$$

- **$pK_b = -\log K_b$**
  - **K_b is inversely related to pK_b**
  - **Larger K_b → smaller pK_b → more ionization → stronger base**

❖ Measurements of concentration

- We use concentration (**Molarity**) to express solutions
- In a **molar solution** → 1 liter of solution contains the number of grams equal its molecular weight → in other words: it is a <u>solution with concentration of 1 Molarity</u>

Molarity (M) **= Number of moles / Volume** (L)

Number of moles = Mass (gram) **/ MW** (gram/mole)

- **<u>Example:</u>** How many grams do you need to make 5M NaCl solution in 100 ml (MW 58.4)?
  - 29.29 g

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- We use **Equivalent** (Eq) to express acids, bases & ions

Equivalent in acids and bases

- It is the <u>number of moles</u>
  - 1 mol of HCl = 1 mol of $[H^+]$ = 1 Eq
  - 1 mol of NaOH = 1 mol of $[OH^-]$ = 1 Eq
- If we have a multi-protic acid → it should be multiplied by the number of moles of the proton
  - 1 mol of H_2SO_4 = 2 mol of $[H^+]$ = 2 Eq

Equivalent in ions

- The mass of an equivalent of ion (g-Eq) is <u>number of grams</u> divided by its charge
  - 1 equivalent of Na^+ → **23.1** g
  - 1 equivalent of Cl^- → **35.5** g
  - 1 equivalent of Mg^{+2} → 24.3/2 = **12.15** g

- **<u>Important note:</u>**
  - ➢ 1 Eq of any acid neutralizes 1 Eq of any base
  - ➢ Titration = neutralization → we need the same equivalence of both substances

- **<u>Example:</u>** Calculate milligrams of Ca^+ in blood if total concentration of Ca^{+2} is 5 mEq/L:
  - ➢ 100 mg/L

- **<u>Example:</u>** Titration of a 12.0 mL solution of HCl requires 22.4 mL of 0.12 M of NaOH, what is the molarity of HCl ??
  - ➢ 0.224 M

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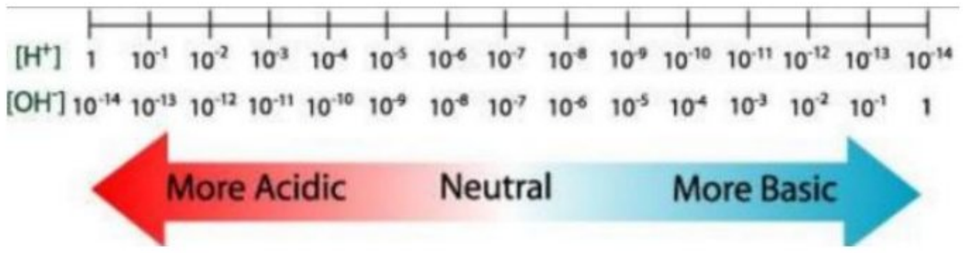
❖ Ionization of water

- Water dissociate to a slight extent to form hydronium ($H3O^+$) & hydroxyl (OH^-) ions
  - ➢ $H_2O \leftarrow\rightarrow H^+ + OH^-$
  - ➢ We can refer to hydronium ion (H_3O^+) as a Hydrogen ion (H^+)



- **$K_w = [H_3O^+] . [OH^-]$**
  - ➢ K_w is the equilibrium constant of water
  - ➢ **$K_w = 1 X 10^{-14}$**
  - ➢ This formula is derived by 2 ways → (K_a X K_b) or (using K_{eq} of water which equals $1.8 X 10^{-16}$)
  - ➢ Note: $[H_2O] = 55.6$ mol/liter

  - ➢ So the product of multiplying $[H_3O^+]$ with $[OH^-]$ must equal 10^{-14} in **any solution** (not only water)
  - ➢ Because **Pure water** is neutral → **$[H^+] = [OH^-]$** = $(10^{-14/2})$ = **10^{-7} M**
  - ➢ If we add an acid → $[H^+]$ increases → the $[OH^-]$ decreases ➔ they are **inversely related**

- **Note:**
  - ➢ **Strong acids:** HCl, HBr, HI, HNO_3, $HClO_4$, H_2SO_4
  - ➢ **Strong bases:** LiOH, NaOH, KOH, $Ca(OH)_2$, $Ba(OH)_2$, $Sr(OH)_2$

- **Examples:**

1) Find the Ka of a 0.04 M weak acid HA whose $[H^+]$ is 10^{-4}:

  - ➢ $K_a = 2.5 X 10^{-7}$

2) What is the $[H^+]$ of a 0.05 M $Ba(OH)_2$:

  - ➢ $[H^+] = 10^{-13}$

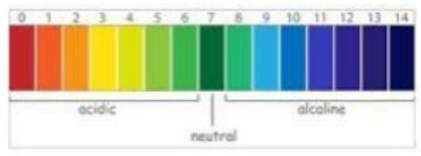
3) $[H^+]$ of a 0.03 M weak base solution is 10^{-10} M, calculate pK_b:

  - ➢ $pK_b = 6.48$

❖ pH

- It is a logarithmic scale of the concentration of proton (H^+)
  - ➢ **$pH = - \log [H^+]$ →→→ $[H^+] = 10^{-pH}$**
  - ➢ As the **pH is smaller** → **more protons** (H^+) → the solution is **more acidic**
  - ➢ A change in the pH by 1 unit implies a **10-fold** difference in the $[H^+]$
    - ✓ A difference of 0.5 pH unit → $[H^+]$ will differ by $10^{0.5} = 3$ times
    - ✓ Lemon juice pH = 2.0, Orange juice pH = 4.0
    - ✓ Urine is more acidic in females (pH = 5) than in males (pH = 8)
    - ✓ Gastric juice is acidic (pH = 1.2-3), and pancreatic fluid is alkaline (pH = 8)

- To determine pH we use: [pH = 0 < acids > 7 , Neutral = 7 , 7 < base > 14]
  - ➢ **Acid-base indicators (**such as litmus paper [the least accurate], universal indicator**)**
  - ➢ **Electronic pH meter (**the most accurate**)**



- **Example:** What is the pH of:
  - ➢ 0.01 M HCl ➔ pH = 2
  - ➢ 0.01 N H_2SO_4 ➔ pH = 1.7
  - ➢ 0.1 N NaOH ➔ pH = 13
  - ➢ 10^{-11} M HCl ➔ pH = 7
  - ➢ 0.1 M of acetic acid ➔ pH = 2.9

    Ka of acetic acid = $1.8 X 10^{-5}$

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❖ Henderson-Hasselbalch Equation:

$$pH = pKa - \log \frac{[\ HA]}{[A^-]} \quad \text{OR} \quad pH = pKa + \log \frac{[\ A^-]}{[HA]}$$

- According to this equation we can define **pK_a** as → the **pH where 50% of acid is dissociated into conjugate base**

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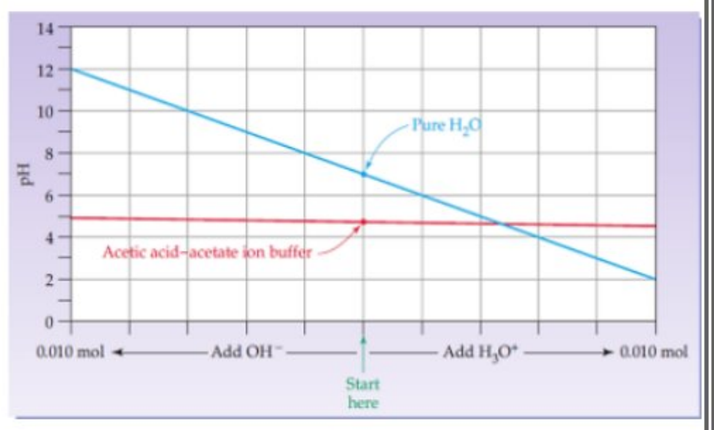
❖ A comparison of the change in pH



- 0.010 mol of base are added to 1.0 L of pure water and to 1.0 L of a 0.10 M acetic acid 0.10 M acetate ion buffer, the pH of the water varies between 12 and 2, while the pH of the buffer varies only between 4.85 and 4.68

- **What is a buffer?**
  - ➢ It is a solution that resists changes in pH by <u>changing reaction equilibrium</u>
  - ➢ They are composed of **<u>mixtures</u> of a weak acid** and a roughly equal concentration of its **conjugate base** (not a weak acid alone, not a conjugate base alone)

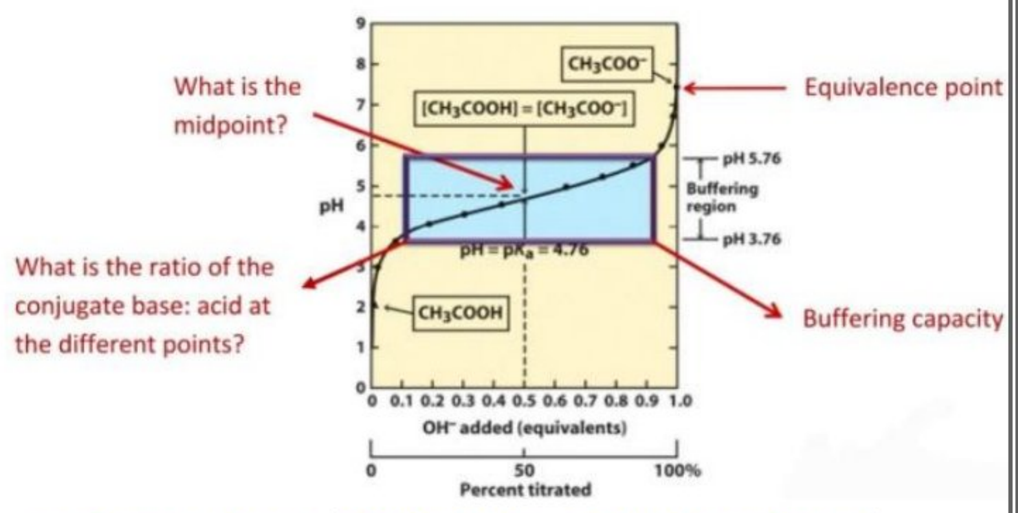
Acid	Conjugate base
CH_3COOH	CH_3COONa ($NaCH_3COO$)
H_3PO_4	NaH_2PO_4
H_2PO_4- (or NaH_2PO_4)	Na_2HPO_4
H_2CO_3	$NaHCO_3$

❖ Titration curve of buffer

- **<u>Note:</u>**
  - ➢ **At low pH:** acids present in the <u>protonated</u> form (acid form)
  - ➢ **At high pH:** acids present in the <u>deprotonated</u> form (conjugated base)

- At the beginning → pH is very low → adding a base to the solution → decreases $[H^+]$ & increases $[OH^-]$ → **pH increases dramatically**

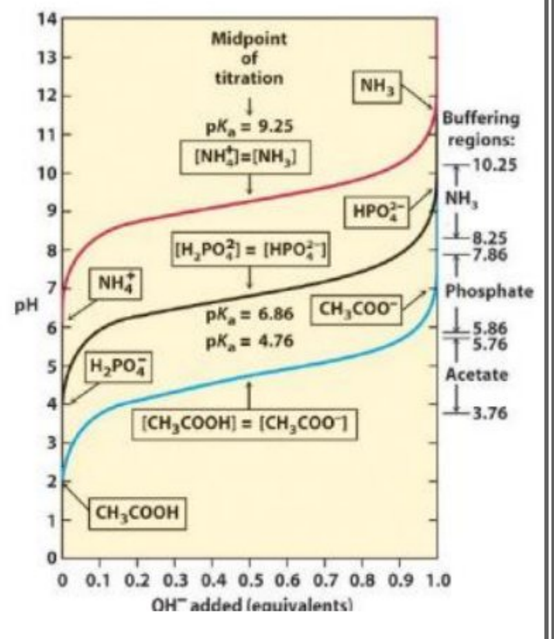
- As pH is increasing → CH_3COOH (a weak acid) tries to resist the change in pH by producing H^+ ions (**increasing the concentration of H^+ and the conjugate base**)



- When the concentration of the **acid =** the concentration of the **conjugate base** (**50% of the acid dissociated**) so **pH reached the value of pK_a** ➔ this point is called **Midpoint** or **Reflection (inflection) point** (because the curve reflects its concavity around this value)
  - ➢ The **region** where the buffer can **manage and resist the changes** in pH is called **Buffering capacity** and it ranges between pH values { **(pK_a – 1) & (pK_a + 1)** }
  - ➢ If we added a buffer in <u>very high concentration</u> → it could manage pH changes in ranges out of it capacity

- As the acid continues deprotonating, its concentration is decreasing → there will be a **low amount of protons to <u>be donated</u>** → so its ability to resist the changes of pH decreases → **pH increase dramatically** (again) → until reaching the **Equivalence point** where almost all of the acid is deprotonated (converted into **conjugate base**)

- **How do we make/choose a buffer?**
  - ➢ A buffer is made by combining weak acid/base and its salt (conjugate)
  - ➢ The ability of a buffer to function depends on:
    - **Buffer concentration**
    - **Buffering capacity** ➔ Which depends on the **pK_a of the buffer** (<u>pH desired</u> should be in the range of the buffer capacity)



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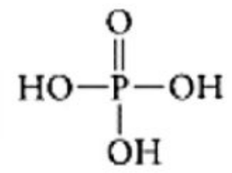
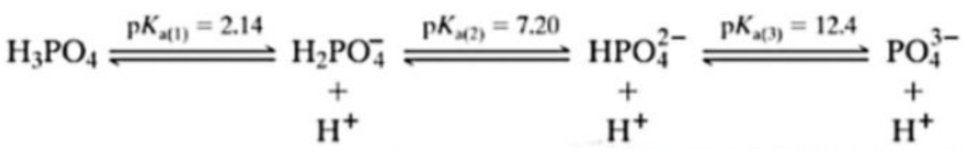
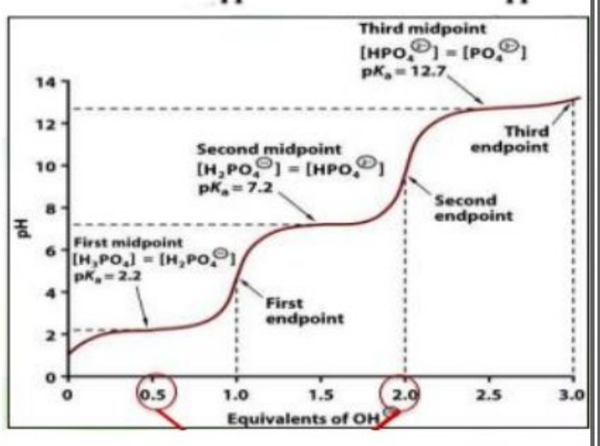
- **Examples:**
  1) **A solution of 0.1 M acetic acid and 0.2 M acetate ion. The pKa of acetic acid is 4.8 calculate pH:**
     - **pH = 5.1**
  2) **Calculate (predict) the pH of a buffer containing**
     - **0.1M HF and 0.12M NaF? (Ka = 3.5 x 10^{-4})**
       - **pH = 3.5**
     - **0.1M HF and 0.1M NaF, when 0.02M HCl is added to the solution?**
       - **pH = 3.3**
  3) **What is the pH of a lactate buffer that contains 75% lactic acid and 25% lactate? (pKa = 3.86)**
     - **pH = 3.38**
  4) **What is the concentration of 5 ml of acetic acid knowing that 44.5 ml of 0.1 N of NaOH are needed to reach the end of titration of acetic acid?**
     - **[CH_3COOH] = 0.89 M**



- **Multi-protic buffers** ➔ such as <u>phosphate buffer</u>
  - Donates their protons gradually and each **<u>donation has different strength</u>** → **different pK_a**
  - The least pK_a is for the first dissociation (the strongest)
  - These buffers are important because they can manage a wide range of pH values





- **Examples:**
  1) **What is the pK_a of a dihydrogen phosphate buffer when pH of 7.2 is obtained when 100 ml of 0.1 M NaH_2PO_4 is <u>mixed</u> with 100 ml of 0.1 M Na_2HPO_4?**
     - **pKa = 7.2**
  2) **A solution was prepared by dissolving 0.02 moles of acetic acid (pKa = 4.8) in water to give 1 liter of solution**
     - **A) What is the pH?**
       - **pH = 3.2**
     - **B) To this solution was then added 0.008 moles of concentrated sodium hydroxide (NaOH). What is the new pH? (In this problem, you may ignore changes in volume due to the addition of NaOH)**
       - **pH = 4.6**

❖ Buffers in human body (Biological buffers)

- The major buffer in the **blood** → **Carbonic acid-bicarbonate** system
- **Dihydrogen phosphate-monohydrogen phosphate** system (**intracellular**)
  - ATP, glucose-6-phosphate, bisphsphoglycerate (RBC)
- **Proteins** (**extra & intracellular**):
  - All proteins can act as buffers → due to the **free carboxyl group** (which accepts & releases H^+ at low pH values) & the **free amino group** (which accepts & releases H^+ at high pH values)
  - **Histidine and cysteine** amino acids → act as buffers
  - Example: <u>Hemoglobin in blood</u>

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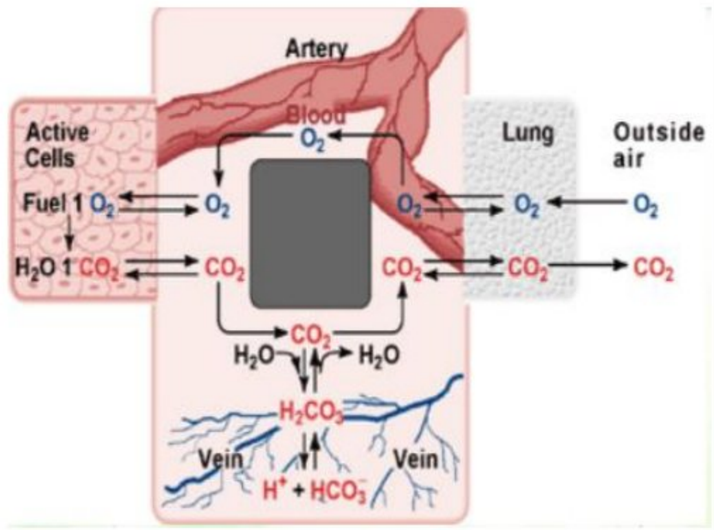
- **Bicarbonate buffer:**
- Bicarbonate buffer interacts with other systems (such as respiratory and renal systems)

$$CO_2 + H_20 \rightleftharpoons H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$$



- **<u>CO_2</u>** dissolves in water (in the lungs) ➔ then in **red blood cells** (RBC) it will be converted into **<u>carbonic acid</u>**
- Carbonic acid then dissociate instantaneously into **H^+ and <u>bicarbonate</u>** in the blood
  - ➢ Carbonic acid is made from CO_2 which can be excreted (rapidly) by exhalation from the lungs
  - ➢ Bicarbonate is excreted via kidneys (slowly → hours to days)

- The **normal blood pH is 7.4** (7.35 - 7.45), and the bicarbonate **buffer capacity is (5.1 – 7.1 / pK_a = 6.1)** so it is far 0.3 units from the normal value. So, how could this buffer be effective??
  - ➢ This buffer has a relatively **high concentration** in the ECF and blood
  - ➢ The components of this system are under the **physiological control** (CO_2 by the lungs, bicarbonate by the kidneys)
  - ➢ Also because it is an **open system** (and can continuously interact with the environment)

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❖ Acidosis & Alkalosis

- pH in the body must be maintained in the normal range, if pH value increased or decreased than this range → that would lead to pathological conditions (Acidosis & Alkalosis)
  - ➢ **Acidosis** → increase the acidity → pH decreases the normal range → **blood pH < 7.35**
  - ➢ **Alkalosis** → More Alkaline environment → pH increases → **blood pH > 7.45**

- They can be due to **Respiratory** or **Metabolic** reasons

Respiratory

Due to disorders & changes in the **respiratory system** → affecting the **concentration of CO_2**

- ➢ **Increasing [CO_2]** → more formation of carbonic acid → more dissociation forming proton & HCO_3^- → more acidity than normal → **Acidosis**
  - ✓ Pulmonary diseases (Asthma, Emphysema, COAD)
  - ✓ Choking, Bronchopneumonia
- ➢ **Decreasing [CO_2]** → the reaction goes in the opposite direction → carbonic acid dissociates into CO_2 and water → proton decreases → **Alkalosis**
  - ✓ Hyperventilation (Anxiety, Hysterical over-breathing, Mechanical over-ventilation)
  - ✓ Raised intra-cranial pressure

Metabolic

Due to changes in the **metabolism** (building and breaking molecules) ➔ any system other than respiratory → affecting the **concentration of H^+**

- ➢ **Increasing [H^+]** → lowering pH → **Acidosis**
  - ✓ Increased production of ketone bodies (starvation, uncontrolled diabetic patients)
  - ✓ Increased production or ingestion of H^+
  - ✓ Impaired excretion of H^+
  - ✓ Loss of HCO_3^- (renal system)
- ➢ **Decreasing [H^+]** → by decreasing acids and increasing bases → increasing pH → **Alkalosis**
  - ✓ Excessive administration of salts & Alkali ingestion
  - ✓ Loss of H^+ (in vomit)
  - ✓ Potassium deficiency

❖ Compensation

- It is the change in HCO_3^- or pCO_2 that results from the primary event
- The process in which we **try to bring pH to the normal ranges**
  - ➢ According to Henderson equation → pH = Pka + log (A^-/HA) → we have to return the ratio of the conjugate base / Weak acid to normal

- If the **problem is metabolic** → the **compensation must be respiratory** and vise versa
  - ➢ **Respiratory acidosis** → **High** pCO_2 → compensated by **increasing** HCO_3^-
  - ➢ **Metabolic acidosis** → **low** HCO_3^- → compensated by **decreasing** pCO_2
  - ➢ **Respiratory Alkalosis** → **low** pCO_2 → compensated by **decreasing** HCO_3^-
  - ➢ **Metabolic Alkalosis** → **High** HCO_3^- → compensated by **increasing** CO_2

- Compensation can be
  - ➢ **Complete** ➔ bringing pH to the normal pH range and limits (7.35 – 7.45)
  - ➢ **Partial** ➔ pH still outside the normal limits
- Complete & partial compensation have the same mechanism but they differ in their ability to return the pH to the normal ranges

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